



PATENT SPECIFICATION

NO DRAWINGS

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Classification:—C08f.

CORRECTION OF CLERICAL ERROR

SPECIFICATION NO. 857,514

The following correction is in accordance with the Decision of the Assistant Comptroller acting for the Comptroller-General, dated the seventeenth day of May, 1961:—

Page 1, line 1, after "We" insert "BERGER, JENSON & NICHOLSON LIMITED, formerly known as"

THE PATENT OFFICE,
12th June, 1961

DS 93401/1(4)/R. 153 200 6/61 PL

15 in-water useful in the process for the decorative coatings and to a process for the emulsion polymerization of one or more of said polymerizable organic compounds.

20 More particularly, this invention relates to an improvement in the combination of ingredients co-acting in aqueous media to provide a favourable environment for free radical polymerization of one or more ethylenically unsaturated polymerizable monomers.

25 One object of this invention is to provide an aqueous medium in which emulsion polymerization reactions may be carried on to form homopolymers, copolymers, terpolymers and other interpolymers of ethylenically unsaturated monomers without excessive foaming, in a predetermined range of particle size useful to deposit of themselves, or after plasticizing, continuous solid films for protective and decorative coatings use.

30 It is a further object to provide a process for producing emulsion polymers of the oil-in-water class which are of improved stability as to age, as to dilution capacity and freeze-thaw cycling in liquid dispersed form and of im-
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weight of the aqueous medium.
The invention also provides a process for the production of polymers and copolymers of ethylenically unsaturated polymerisable organic compounds which comprises heating one or more of said polymerizable organic compounds in dispersion in the above-described aqueous medium whilst maintaining the dispersed state of agitation of the reaction mixture.

60 This invention further provides an oil-in-water emulsion the disperse phase of which comprises a polymer of vinyl acetate or a copolymer thereof with a minor proportion of one or more other ethylenically unsaturated monomers and the continuous phase of which comprises an aqueous solution of a non-ionic protective colloid consisting of polyvinyl alcohol of at least 95% hydrolyzed quality or hydroxyethyl cellulose or admixtures thereof, a water-soluble non-ionic emulsifying agent, containing a plurality of oxyethylene groups, having a hydrophilic number of from 65 to 75 and a quantity of an acetylenic, ditertiary

Price 4s. 6d.

PATENT SPECIFICATION

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International Classification:—C08f.

COMPLETE SPECIFICATION

Improvements in or relating to the production of Emulsion Polymers and Aqueous Media therefor

We, LEWIS BERGER & SONS LIMITED, a British Company, of Berger House, Berkeley Square, London, W.1, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a universal aqueous medium in which ethylenically unsaturated polymerizable organic compounds may be emulsified and polymerized to form relatively high molecular weight dispersions of polymers-in-water useful in film-forming protective and decorative coatings and to a process for the emulsion polymerization of one or more of said polymerizable organic compounds.

More particularly, this invention relates to an improvement in the combination of ingredients co-acting in aqueous media to provide a favourable environment for free radical polymerization of one or more ethylenically unsaturated polymerizable monomers.

One object of this invention is to provide an aqueous medium in which emulsion polymerization reactions may be carried on to form homopolymers, copolymers, terpolymers and other interpolymers of ethylenically unsaturated monomers without excessive foaming, in a predetermined range of particle size useful to deposit of themselves, or after plasticizing, continuous solid films for protective and decorative coatings use.

It is a further object to provide a process for producing emulsion polymers of the oil-in-water class which are of improved stability as to age, as to dilution capacity and freeze-thaw cycling in liquid dispersed form and of improved durability against re-emulsification when in a deposited, dry-film form.

According to the present invention there is provided an aqueous phase reaction medium which comprises a dilute aqueous solution of a non-ionic protective colloid, a water-soluble non-ionic emulsifying agent containing a plurality of oxyethylene groups wherein the effective balance between lipophilic and hydrophilic ends of the molecule characterizes the emulsifying agent as having a Hydrophilic Number (hereinafter abbreviated to HN) of 65 to 75 and one or more acetylenic, ditertiary alcohols in an amount not exceeding 1% by weight of the aqueous phase.

The invention also provides a process for the production of polymers and copolymers of ethylenically unsaturated polymerisable organic compounds which comprises heating one or more of said polymerizable organic compounds in dispersion in the above-described aqueous medium whilst maintaining the dispersed state of agitation of the reaction mixture.

This invention further provides an oil-in-water emulsion the disperse phase of which comprises a polymer of vinyl acetate or a copolymer thereof with a minor proportion of one or more other ethylenically unsaturated monomers and the continuous phase of which comprises an aqueous solution of a non-ionic protective colloid consisting of polyvinyl alcohol of at least 95% hydrolyzed quality or hydroxyethyl cellulose or admixtures thereof, containing a plurality of oxyethylene groups, having a hydrophilic number of from 65 to 75 and a quantity of an acetylenic, ditertiary

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alcohol not exceeding 1% by weight of the aqueous phase.

5 In the general practice of the invention, a stock solution (of from 1 to 10% concentration) of a non-ionic protective colloid, preferably a fully hydrolyzed polyvinyl alcohol, is prepared by dissolving the protective colloid in water at 150° to 195° F.

10 A jacketed resin kettle equipped with a reflux condenser, thermometer, sealed variable-speed motor-driven agitator, inert gas inlet, monomer inlet and an additional inlet for metering in of catalyst in liquid form provides suitable apparatus for conducting the polymerization reactions of this invention.

15 If monomers which are gaseous at room temperature are contemplated, means for pressurizing the system are essential. It is preferred to use a pump to circulate hot water through the exterior jacket of the resin kettle and to provide means to switch to cold water quickly should the reaction become highly exothermal and tend to get out of control.

20 The stock aqueous solution of protective colloid is charged to the kettle together with the acetylenic alcohol or alcohols and the non-ionic emulsifying agent and the interior of the kettle purged with nitrogen. Further, it is preferred to maintain a nitrogen blanket over the reactants throughout the reaction period. Solution of the protective colloid can be accomplished at this point if one so elects. The temperature of the colloid-water dispersion is raised to 150° to 175° F. in one procedure before any monomer addition is made.

25 The method of addition of the monomer or blend of monomers controls the particle size range of the final polymerized disperse particles to a great extent. It is preferred to seed the reaction with a small quantity of previously-prepared emulsion of the same quality and particle size before introducing the monomer.

30 First, assume the desire is to produce a fine particle size product. After seeding the aqueous reaction medium at 150°—175° F., a small amount of sodium bicarbonate is added and a part (one-third in the case of a vinyl acetate homopolymer) of the peroxide free-radical catalyst is added. Thereafter, the monomer is fed into the aqueous reaction medium at a rate sufficient to maintain a slight or gentle reflux of monomer. If reflux continues for more than a few minutes after monomer addition is stopped, additional increments of a free radical catalyst are added (10% of total has been used with good results) to re-activate. In the case of vinyl acetate homopolymerization, for example, the temperature will not exceed about 185° F., nor fall below about 165° F. After all of the monomer has been added, the temperature is increased and refluxing substantially stops. Additional time at slightly above reaction temperature subsequent to this period is bene-

ficial. Rapid cooling of the emulsion polymer should be avoided.

70 If a relatively coarse particle size emulsion is desired, the result may be obtained by adding the entire quantity of monomer at the start. The catalyst is held back, using approximately one-third of the total catalyst with the monomer charge. The temperature of the aqueous reaction medium at the start is preferably below 150° F. and is raised slowly after monomer addition to a moderate reflux rate. The resultant exothermic reaction which ensues is controlled by running cooling water through the vessel jacket and by careful control (slowing down) of the rate of catalyst addition. Start of vigorous reflux serves as a signal to curtail the reaction rate in the vessel by cooling. After all catalyst has been added and the reflux rate again slows to a practical stop, the temperature of the reaction mass is allowed to increase to a value below the boiling point of water and preferably not above about 190° F. for about a half-hour. The best practice is, at the end of the reaction, to filter the batch to remove any coagulum and to vacuum distil the product before it cools down to remove the last traces of monomer. Residual monomer to the extent of $\frac{1}{2}\%$ and more in the final emulsion polymer has been found to contribute to product instability.

95 An improved technique of large particle size production utilizes a variation over that set forth above. Advantage resides in better thermal control during production. In this process the jacketed vessel is seeded with a large particle size pre-formed emulsion. The protective colloid, water, about one-third of the total catalyst and ditertiary acetylenic alcohol is combined with the pre-formed emulsion polymer. Approximately one-third of the total non-ionic emulsifying agent and the monomer or blend of monomers is added and emulsified into the aqueous medium at 150°—160° F. When reflux slows down after holding at about 185° F. another one-third of the emulsifying agent and another one-third of monomer is added along with a proportionate amount of catalyst. The time-temperature reflux conditions of the first step are repeated. Again, after reflux becomes impractically slow, the final one-third of emulsifier, monomer and catalyst are added to the reaction mass and the same conditions repeated a third time. It has been determined by the work herein described that the ratio of monomer to fresh emulsifying agent is important in control of particle size. Generally, the larger amount of monomer to smaller amount of emulsifying agent during the first few minutes of polymerization leads to larger particle size products, the reverse also holding true, namely; small amount of monomer to large amount of emulsifying agent leads to fine particle size products. Control of particle size of the disperse oil phase appears, from data at present available, to be of par-

tical advantage in coating compositions.

A secondary procedure provides an alternative method. In this process the aqueous phase is seeded. About 10% of the total monomer charge is added to the aqueous reaction medium (at about 160° F.) plus about one-third of the total catalyst. The reaction medium is allowed to reflux slowly until the reflux rate approaches zero. At that time further increment additions of monomer and catalyst are carried out, maintaining the slow reflux rate. These steps are repeated until all monomer is reacted and reflux ceases.

A third and preferred procedure, giving rise to products of intermediate particle size of dispersed polymer phase has been found most adaptable to large scale production. Such products have the advantage of 1) freeze-thaw cycle quality of the larger particle size emulsions; 2) adhesive properties of larger size particles; 3) water resistance of the dry film of small particle size emulsions; 4) dilution and shelf stability of the fine particle size products. This third procedure is described and illustrated with specific relation to vinyl acetate homopolymers in Example 3 which follows. The same procedure is both applicable to and advantageously used in producing copolymers, terpolymers and higher interpolymers by obvious modification in monomer content.

Having thus described the invention generally, the following Examples, in which the percentage figures are calculated by weight, are included as illustrative of various homopolymers, copolymers and terpolymers in the formation of which the aqueous reaction medium here described has been advantageously employed in the manufacture of emulsion coating compositions.

EXAMPLE 1 VINYL ACETATE HOMOPOLYMER (Small particle size)

Into a two-litre resin kettle equipped with a reflux condenser, thermometer, sealed variable-speed motor-driven stirrer, nitrogen blanket tube and two dropping funnels were weighed 875 grams of a 4% aqueous solution of a 98% hydrolyzed quality polyvinyl alcohol of two viscosity grades (50% Elvanol 72-60 and 50% Elvanol 70-05), 0.5 gram dimethyl octynediol, 17 grams gum arabic and 17 grams of a polyethylene glycol alkyl ether having an HN number of about 74 ("Tergitol" (Registered Trade Mark) Dispersant XC Carbide and Carbon Chemicals). The reaction vessel was purged with nitrogen and the reaction medium heated to 150° F. to assist solution of the gum arabic. At 175° F. an addition was made of 2 grams sodium bicarbonate and 2 ccs. of 29% hydrogen peroxide from one dropping funnel. 672 grams of freshly distilled vinyl acetate monomer were weighed into the

other dropping funnel and the cock was opened sufficiently to allow slow addition of the monomer and the rate of monomer and hydrogen peroxide addition were regulated so that gentle reflux persisted and the temperature did not exceed 180° F. nor fall below 165° F. Reflux should stop within a few minutes after monomer addition is cut off. If this does not occur, additional free radical catalyst (hydrogen peroxide) is added in 1 cc. increments, 6 ccs. of peroxide is usually sufficient for the entire reaction. When all the vinyl acetate monomer has been added, refluxing subsides and the batch temperature is increased to about 190° F. The batch is held at this temperature for 30 minutes. Thereafter, the heat input is discontinued and the batch cooled slowly. Agitation is continued throughout the heating and cooling period at a relatively slow rate.

The emulsion polymer product has a pH of between 3.5 and 6, will not settle in 24 hours though diluted 900% with distilled water and will not coagulate after 3 cycles of freezing at -10° F. and thawing at room temperature.

Pre-seeding the reaction medium with a similar product, previously made, is suggested to obtain optimum product quality.

EXAMPLE 2

VINYL ACETATE HOMOPOLYMER (Large particle size)

Equipment and formulae are the same as in Example 1 except that 12 grams of the non-ionic emulsifier were used. In this process, after addition of 2 ccs. of catalyst to initiate the reaction, all of the vinyl acetate monomer is added to the aqueous reaction medium at one time.

Due care should be exercised in supplying heat to the reaction mass. Monomer reflux starts at about 150° F. whereupon the reaction proceeds exothermically at such rate that cooling water must often be fed through the outer jacket to prevent too violent a reaction. Additional catalyst is added in small increments, after refluxing slows, until 6 ccs. in total have been added.

When the reaction has been completed, the temperature is held at 190° F. for 30 minutes and the final emulsion product subjected to vacuum treatment, while still hot, to remove traces of monomer. Not only do residual amounts of monomer contribute to odour, but in quantities over ½%, excess monomer contributes to emulsion instability. The dispersed particle size of the resulting emulsion homopolymer range from 5 to 30 microns in diameter.

It is general practice to increase the non-ionic polyoxyethylene containing emulsifier content slightly when making fine particle size products (e.g. 1.5% on the water present is useful) and to reduce the emulsifier content,

for example to about 0.6%, when producing large particle size products.

EXAMPLE 3

VINYL ACETATE HOMOPOLYMER

5 Preferred Method—Intermediate particle size

In this procedure, the aqueous solution of the non-ionic protective colloids is prepared and the vinyl acetate monomer is emulsified therein by means of the water-soluble non-ionic emulsifying agent. The emulsified monomer is transferred to the dropping funnel leading to the reaction vessel. The reaction vessel is charged with a quantity of a previously-prepared emulsion homopolymer of about one-fifth the total weight of the batch to be made. Temperature of the seed charge is elevated to about 150° F. The alkali bicarbonate and 2 ccs. of hydrogen peroxide are added to the seed charge to promote polymerization. 10% of the total of emulsified monomer in the dropping funnel is added to the emulsified polymer seed charge in the reaction vessel. The temperature is raised to provide a gentle reflux rate. Use of the seed charge is not essential, but provides a useful technique. Reflux rate is maintained until the temperature reaches 175° F. and reflux stops. Again an addition of 10% of the total emulsified monomer is added, slowly, together with sufficient catalyst to maintain reflux conditions. Slow, stepwise addition is carried forward until all catalyst (about 6 ccs. in this case) and emulsified monomer have been fed into the reaction medium.

After the last aliquot portion of emulsified monomer and free radical catalyst have been added and reflux substantially ceases, the temperature is increased to 185°—195° F. and held for 30 minutes. Final traces of monomer are removed and the product concentrated to about 45% monomer solids under vacuum while the batch is hot.

The particle size of the product is intermediate between that obtained in prior examples. The spread between large and small particles may range between 0.5 micron and 20 to 30 microns.

Advantages of both methods and particle size ranges are obtained. Freeze-thaw stability and adhesive properties of large particle size emulsions together with water resistance, dilution stability and shelf stability of the fine particle size process is obtained.

The above technique is equally applicable to the manufacture of copolymers, terpolymers and other interpolymers of ethylenically unsaturated monomers in producing oil-in-water emulsion polymers for use in the coatings art.

EXAMPLE 4

COPOLYMER PRODUCTION Vinyl acetate-dibutyl maleate

60

The equipment described in Example 1 was used. An aqueous solution was prepared containing 70 grams of a high molecular weight fully hydrolyzed polyvinyl alcohol, 17 grams of gum arabic, 17 grams of an ethylene oxide addition product emulsifier having an HN value of 74 (Tergitol XC), 0.5 gram dimethyl octynediol, 2 grams potassium bicarbonate in 905 grams water. In general, the method of Example 1 was followed. A monomer blend containing 572 grams of vinyl acetate and 100 grams of dibutyl maleate was prepared and transferred to the dropping funnel. 2 grams of potassium persulphate in 4 grams water was added to the charge, meanwhile the reaction vessel was purged with nitrogen. The reaction mass was heated to 150° F. The stop-cock was opened sufficiently to allow slow addition of the monomer blend. 1 cc. additions of 10% aqueous solution of the alkali persulphate were made if reflux continued long after monomer addition was curtailed. The procedure was followed until all the monomer blend and an equivalent of about 5 grams total of potassium persulphate had been added. After the last addition of catalyst and monomer and arrest of reflux, the temperature was increased to about 190° F. The batch was held at this temperature for about 30 minutes. Traces of monomer were vacuum stripped from the copolymer emulsion and the concentration of polymer solids in the emulsion increased to about 45% by water evaporation.

This product, as well as other copolymers set forth in the following Table, were formulated into emulsion paints for exterior exposure tests as well as other routine tests to determine comparative quality of the copolymerized film-forming components for a number of specific end uses, including fabric and paper coatings, primer for fresh plaster, interior wall finishes and industrial finishing applications.

Table I sets forth a series of copolymers produced in a similar manner to the emulsion copolymer described in Example 4 (with minor variations in free radical catalyst, non-ionic emulsifying agent containing a plurality of oxyethylene groups between an HN value of 65 and 75 and in the symmetrical acetylenic ditertiary alcohol selected). Variations were made within limitations hereinafter described in greater detail. The examples, while numerous, are not exhaustive of the potential combinations of ethylenically unsaturated monomers useful in accordance with this invention.

TABLE I

Principal Monomer	Minor Monomer	Weight Ratio Principal-Minor Monomer
Vinyl Acetate	Dibutyl fumarate	90:10
"	Dibutyl itaconate	85:15
"	Dibutyl maleate	85:15
"	"	85:15
"	Vinyl 2-ethylhexoate	85:15
"	Vinyl propionate	75:25
"	2-ethyl hexyl acrylate	90:10
"	n-vinyl pyrrolidone	85:15
"	Vinyl stearate	85:15
"	Diisooctyl fumarate	85:15
"	Diisooctyl maleate	85:15
"	Dioctyl maleate	85:15
"	Dioctyl fumarate	85:15

TERPOLYMER PRODUCTION

Again, in equipment as used and described in Example 1, a comprehensive series of terpolymers were produced as identified in Table II. The methods described in Examples 1, 2 and 3 were tried with favourable result obtained following the general procedure of Examples 3 and 4, namely; by pre-emulsification of the monomer blends in the aqueous reaction medium prior to polymerization by means of the free radical catalyst and catalyst activator in the reaction vessel. Here, the specific end use for which the product was intended required fine particle emulsion terpolymers.

While it is possibly unnecessary to describe a representative procedure in view of the examples of homopolymerization and copolymerization heretofore set out, some improvement has been observed in the quality of emulsion terpolymers obtained by a minor change in the non-ionic protective colloid used in the reaction medium combination. While satisfactory products are obtained without changing the colloid, in this instance one may substitute all or a part of the polyvinyl alcohol with a water soluble hydroxyethyl cellulose. This cannot be done in the homopolymer and copolymer with correlative improvement. In fact, only with correlative loss in quality. It

is to be noted that in the case of the terpolymer condensations all of the polyvinyl alcohol may be replaced with hydroxyethyl cellulose without loss in quality of the final oil-in-water emulsion polymer system.

EXAMPLE 5

Into equipment as described in Example 1 were weighed 840 grams of water, 17.5 grams of hydroxyethyl cellulose (of a quality which at 5% concentration in water yields a solution of 50—150 centipoises at 20° C.) and 17.5 grams of hydroxyethyl cellulose (of a quality which under the same conditions yields a solution of about 30-thousand centipoises), 0.5 gram of dimethylhexyne diol, 17 grams of an alkyl aryl polyethylene glycol ether ("Tergitol" NPX) having an HN value between 65 and 75 and 2 parts of potassium bicarbonate. The aqueous mixture was heated at a temperature of about 150° F. to produce a homogeneous solution. A blend of monomers consisting of 538 grams of vinyl acetate, 67 grams of dibutyl maleate and 67 grams of ethyl acrylate was transferred to the dropping funnel and the reaction vessel purged with nitrogen. 2 grams of potassium persulphate in 4 grams of water were added to the aqueous reaction medium. The monomer blend

- was then fed into the aqueous reaction medium at a rate sufficient to maintain a steady drop-wise reflux return of disperse phase reactant to the aqueous reaction medium. The temperature was held at a level below 185° F. during monomer addition. Drop-wise additions of a 10% aqueous solution of potassium persulphate were made during the reaction period. (If reflux stopped upon arresting monomer addition, a drop or two of catalyst was added). A total of 3.2 grams of catalyst were added to complete emulsion interpolymerization of the monomers. After all the monomer had been added, the temperature was held at 185°—190° F. for 30 minutes. Vacuum was applied to the reaction vessel and residual monomer thereby removed.
- In this instance the particle size of the final emulsion product was so fine that there was exhibited a reddish purple fluorescence characteristic of particles in colloidal states of subdivision. Fluorescence from blue-green to violet has been observed in other examples.
- Terpolymer-containing emulsion polymer systems can be made in the various larger particle size ranges, as previously described for homopolymers and copolymers, by variations in technique as has been described herein. Fully hydrolyzed polyvinyl alcohol is equivalent to the hydroxyethyl cellulose in terpolymer formation reactions.
- The following Table II illustrates a few of the many interpolymer systems that have been made in accordance with techniques referred to herein and illustrated in the Examples.

TABLE II

Principal Monomer P	Minor Monomer B	Minor Monomer C	Weight Ratio P:B:C:
Vinyl Acetate	Dibutyl Maleate	Ethyl Acrylate	90:5:5
"	"	"	70:15:15
"	"	"	50:25:25
"	"	"	50:40:10
Vinyl Acetate	Acrylonitrile	Dibutyl Maleate	80:10:10
"	"	2-ethyl-hexyl acrylate	80:10:10
Vinyl Acetate	Dibutyl Maleate	N-butyl acrylate	80:10:10
"	2-ethyl-hexyl acrylate	Dibutyl maleate	80:10:10
Vinyl Acetate	Styrene	Ethyl acrylate	80:10:10
"	Acrylonitrile	Ethyl acrylate	80:10:10
Vinyl Acetate	2-ethyl-hexyl maleate	Ethylene glycol dimethacrylate	85:14:1

- From the above examples it is obvious that combinations containing more than three different monomers offer opportunity for variation in quality of products obtained, affecting the adhesion, toughness, permeability and other factors of moment in the paint industry.
- Organic water-insoluble monomers subject to addition polymerization containing an ethylenic double bond useful in accomplishing the end purpose of this invention, namely, an oil-in-water emulsion polymeric system useful in producing film-forming coatings, are innumerable. The following monomers, all of which may be used in the production of polymer emulsions in accordance with the present invention have been set out in the prior art, either as the sole agent in homopolymeric systems, or in dual combinations to form copolymers, or in combinations of three or more to form increasingly complex high molecular weight condensation products. Representative species of the classes enumerated have been polymerized in the aqueous system herein described with consequent development of emulsion coating compositions suitable for a wide variety of decorative and industrial finishing end uses. Of primary significance are

the polymerizable vinyl monomers including vinyl acetate, styrene, methyl styrene, divinyl benzene, vinyl hexoate, vinyl butyrate, vinyl valerate, vinyl sulphone, vinyl octoate, acrylonitrile, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethyl-hexyl acrylate, tetrahydrofurfuryl methacrylate and vinyl toluene which are characterized by a terminal $\text{CH}_2=\text{C}-$ group. Other useful unsaturated monomers containing an ethylenic double bond are esters of alpha-beta unsaturated dicarboxylic acids and include methyl maleate, ethyl maleate, methyl fumarate, ethyl fumarate, diallyl maleate, methyl-aconitic acid esters, ethyl aconitic acid esters, methyl and ethyl esters of citraconic and itaconic acid, dimethyl amyl maleate, ethylene glycol dimethacrylate and other unsaturated acid esters including those of saturated and unsaturated alcohols containing up to about 16 carbon atoms are known to be useful. In general, the longer the alkyl chain the slower the reactivity, but drying oils wherein the alkyl chain contains 16 or more carbon atoms have been polymerized in emulsion systems.

Still other useful monomers for emulsion polymerization in accordance with this invention include methyl isopropenyl ketone, methyl vinyl ketone, methacrylonitrile, piperylene, allyl acetate, butadiene, isoprene and methyl vinyl ether. If pressure equipment is available even more volatile monomers, for example, ethylene and substituted ethylenes, not liquids at usual emulsion polymerization temperatures but of the general class, are also of economic importance in the production of worthwhile emulsion polymers.

The homopolymers, copolymers, terpolymers and more complex polymers producible in the emulsion systems of this invention are adaptable to many end purposes. The principal end use of moment here for products of this invention is in the protective and decorative coatings art, where the emulsion polymer may be used of itself as a clear coating for paper, cloth, wood and primed metal surfaces. The emulsion polymers may be pigmented to produce requisite colour and gloss, and they may be plasticized, either internally or externally, if desired, to modify the nature of the dry film deposited after evaporation of the aqueous phase.

Coatings containing a major percentage of polyvinyl acetate are at present widely used as coatings for fresh plaster, masonry and other surfaces. They are useful as adhesives, as wood glue, as well as for laminating a variety of substances. Modification of a polymer containing a major percentage of vinyl acetate with one or more ethylenically unsaturated monomers other than vinyl acetate provides means for changing the nature of the final product to enhance various desired qualities including adhesion, resistance to water, organic chemicals, alkali and acid; toughness; solubility and hard-

ness. It is well known that the nature of the aqueous phase strongly influences the quality of product obtained in an emulsion polymer. From the foregoing it is clear that this invention provides improvement in the aqueous phase reaction medium in the emulsion polymerization art.

Because of the ready availability, lack of necessity of pressure reactors and economic advantages offered by vinyl acetate monomer, the specific examples have been confined to products containing at least 50% of vinyl acetate monomer in the dispersed polymer forming phase but this is not to be construed as a limitation upon the diversity of emulsion polymers producible within the scope of this invention.

FREE RADICAL CATALYSTS

The classes of catalysts useful in emulsion polymerization reactions involving ethylenically unsaturated monomers have been fairly thoroughly explored in the prior art and are those classed as free radical catalysts.

Among those commonly used are the peroxides, persulphates and azo-type catalysts. The various water-soluble persulphates include potassium and ammonium persulphate as exemplary. Illustrative peroxides include hydrogen peroxide, benzoyl peroxide, acetyl peroxide, tertiary butyl hydroperoxide and other organic peroxides having more or less solubility in water. Additionally, free radical catalyst activators are commonly employed in conjunction therewith and include sodium bicarbonate, water soluble pyrophosphates and water-soluble iron and cobalt salts.

The prior art indicates free radical catalysts are present and used in polymerization reactions in sufficient quantity to provide from 0.001 to about 0.1 part available oxygen per 100 parts of aqueous reaction medium during monomer interpolymerization.

THE NON-IONIC EMULSIFIER

In the prior art of emulsion polymerization of water-insoluble monomers containing ethylenic unsaturation, little attention has been given to emulsifier selection. In fact, the general picture presented is that all classes of emulsifiers including the anionic agents, illustrated by metal soaps of long chain or high molecular weight organic acids (sodium salts of alkyl aryl sulphonic acids), the cationic agents, illustrated by the quaternary nitrogen containing compounds (lauryl pyridinium chloride), and the non-ionic emulsifying agents, illustrated by the polyalkylene glycol esters of long chain fatty acids are treated as equivalent to each other and equivalently useful in polymerization reactions in emulsion systems.

In studies leading to the present invention it was determined that not only is the general chemical class of emulsifying agent employed

important but the stability with time of the polymer dispersions in water may be remarkably enhanced through correlating the emulsifying agent essential to emulsion polymerization reactions with the nature of the protective colloid and the quality of other adjuvants present in the reaction medium.

In the present reaction medium for emulsion polymerization of ethylenically unsaturated monomers, the quality of the non-ionic emulsifying agents containing ethylene oxide groups chemically combined with oil-soluble (lipophilic groups) groups were found to be a critical part of the total composition. The balance existing between the hydrophilic portion and the lipophilic portion of the non-ionic emulsifying agents was found critical within a relatively narrow range of value. A numerical value, referred to as the Hydrophilic Number or Hydrophile Number and more commonly and simply as the HN number, or HN value, or merely as HN, has been found extremely useful in reducing to an exact description the quality of balance of the hydrophilic and lipophilic portions of non-ionic agents essential to the aqueous emulsion medium herein described. Another terminology used in the emulsion art, referred to as the Hydrophile-Lipophile Balance, or HLB has numerical relation to HN. For practical purposes, they are related by the following simple equation:

$$HN = 5(HLB)$$

Thus, if the HLB of an emulsifier has been established as, for example, 14, then the HN value is approximately 70.

Originally, the HLB values were developed by purely empirical means and have been described in an article by Wm. C. Griffin entitled "Calculation of HLB Values of Non-Ionic Surfactants" (December 1954, Volume V, Number 4, Journal of the Society of Cosmetic Chemists. This paper was based in part upon earlier work of the same author in a paper entitled "Classification of Surface Active Agents" appearing in Volume I, Number 5 of the same Journal for December, 1949.

Briefly stated, the HLB value is "an expression of the relative simultaneous attraction of an emulsifier for water and for oil (or for the two phases of a system to be emulsified). For purposes of convenience the effective balance of these two groups is assigned a numerical value." Under the HLB system of nomenclature those emulsifying agents most lipophilic (or attracted to oil) are given low numbers and those attracted strongly to water are assigned progressively higher numbers. The numerical values range from one to forty with 10 being a practical mid-point of the range.

Further, experience with assignment of numerical physical constants to emulsifiers has established that these values are not limited to ethylene oxide-containing emulsifying agents

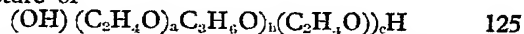
nor to any particular chemical class of emulsifiers but can be assigned to anionic emulsifying agents as well. For example, the well-known sodium salt of dioctyl ester of sulphosuccinic acid has been demonstrated to have a very high Hydrophilic Number, or HN, of about 150. Part of the higher values attributed to this class is believed due to their ionic nature. Indications are that the cationic agents are also of very high HN. One cationic agent, illustratively, possesses an HN value of more than 125.

More recently, another method of determining the HLB or HN value of non-ionic emulsifiers containing ethylene oxide groups has been suggested by Griffin which is based upon the temperature at which turbidity develops in a standard concentration of the non-ionic emulsifying agent of unknown HLB or HN value in water. Turbidity does not always develop so that the method is not entirely universal.

Two non-ionic oxyethylene type emulsifying agents of different but known HLB or HN value are dissolved in a standard quantity of water. Each is separately heated and the temperature of clouding or turbidity development noted. A cloud point temperature—HLB (or HN) graph is developed from the data. For practical purposes, the relationship illustrated by this technique is a straight line function. From an experimentally determined cloud point temperature of the unknown non-ionic emulsifier, an HLB or HN value may be assigned.

It is also understood in the art of emulsification that emulsifying agents of varying HLB or HN may be blended in mathematically calculated quantities to produce blends of emulsifiers of appropriate HLB or HN values intermediate the values of those selected for blending, having a requisite HN value in the combination. It is within the scope of this invention that this method may be employed to produce, by combination of two or more agents, surface-active materials equivalent in HN value to those herein described and claimed.

Having described the general class of emulsifiers suitable for the purposes of this invention, several illustrative ones, preferred for use because they are readily available commercially and are outstandingly useful, are the polyoxyethylated octyl and nonyl phenols and the alkyl polyglycol ethers having HN numbers of between 65 and 75. An additional series of compounds useful for the purposes of the invention have the general chemical structure of



wherein a b and c are numerals of such value that the molecular weight is between 1500 and 1800, the percentage of ethylene oxide groups in the molecule is between 20 and 50% and the HN value is estimated, from cloud point

determinations, to be between 65 and 75.

From the above discussion it may be observed that the nature of the chemical combination and size of lipophilic and hydrophilic groups in non-ionic emulsifying agents will affect the HN value. However, as the concept is a physical one, as previously explained, HN value provides a means of physical definition of the useful sub-classes under the non-ionic emulsifying agent class containing a plurality of oxyethylene groups suitable for the purposes of the present invention.

THE PROTECTIVE COLLOID

Heretofore the emulsion polymerization art relating to monomer compounds containing an ethylenically unsaturated group has disclosed various hydrophilic protective colloids useful in the aqueous phase of emulsion polymerization systems. Among these are sodium carboxymethyl cellulose, water-soluble methyl and ethyl celluloses, hydroxyethyl cellulose, partially hydrolyzed polyvinyl alcohol, gum arabic, gum tragacanth, water-soluble alginates, casein and like substances.

One most commonly suggested is polyvinyl alcohol containing up to about 10% of acetate groups. For the purposes of the present invention it has been found that excessive foaming is reduced, greater shelf stability upon age of the emulsion is obtained, higher reductions of the emulsion with water are permissible, increased mechanical stability (emulsion products will withstand very high shear for extended time periods), greater water-resistance of the dried film, increased resistance to emulsion breakdown by freeze-thaw cycling and lower emulsion viscosities are obtained in the herein recited aqueous phase composition if the protective colloid in the combination described is a polyvinyl alcohol containing at least 95% polyvinyl alcohol and preferably in excess of 98% polyvinyl alcohol or in other words substantially completely hydrolyzed polyvinyl alcohol. In the composition of the invention, more than 5% of polyvinyl acetate in the lyophilic colloid has been found to cause excessive foaming most difficult to control. In emulsion polymerizations of this invention, other protective colloids, such as hydroxyethyl cellulose and gum arabic, may be used to supplement the fully hydrolyzed polyvinyl alcohol in part. Not more than about 50% by weight of the polyvinyl alcohol present may be replaced by such other protective colloid (except in the case of terpolymers) without diminishing the quality of the product. In the case of terpolymers substantially fully hydrolyzed polyvinyl alcohol and hydroxy ethyl-cellulose are equivalent. According to the best

information at hand, the hydroxyethyl cellulose useful in the terpolymer systems contains from about 2 to 2½ ethoxy groups per cellobiase unit.

The total amount of protective colloid present may be varied within practical limits. At the low end of the scale, namely less than two per cent (based on the weight of the total aqueous phase), poor adhesion of films deposited from the emulsion is observable and at greater than 10%, viscosity of emulsion polymers containing from 40—55% emulsified polymer solids, is impractically high for coating purposes.

In specific homopolymers, copolymers and terpolymers some advantages can be obtained by more stringent attention to the quality and quantity of the protective colloid, as will be observed in certain of the previous examples included as illustrative. Synergistic effects between gum arabic and fully hydrolyzed polyvinyl alcohol, for example, have been observed in certain interpolymeric reactions.

THE ACETYLENIC ALCOHOL

A further essential component of the combination found to produce emulsion polymers for coating purposes of improved quality is an acetylenic ditertiary alcohol, preferably symmetrical.

The function of the ditertiary acetylenic alcohols has not been established. Though the quantity useful is within a relatively narrow range, e.g. from trace amounts (of the order of 0.05%) to not more than 1% of the total aqueous phase, the beneficial influence on a wide variety of emulsion polymer systems and emulsion interpolymer reactions has been of outstanding value. Among the advantages noted by their inclusion have been increased stability upon subjecting the system to freeze-thaw cycling tests (so long as the aforementioned range is not exceeded) and lower viscosity of the emulsion system at a given solids polymer concentration.

Dimethyl hexynediol and dimethyl octynediol have been found to be extremely useful at about 0.1% to 0.5% by weight of the aqueous phase. Above 0.6% the advantages diminish and at more than 1% gelation has been observed in some instances after a single freeze-thaw cycle.

The following chart illustrates the advantage of the ditertiary acetylenic alcohols in a series of test runs wherein a straight polyvinyl acetate homopolymer of approximately 42% polyvinyl acetate solids was produced. Various quantities of dimethyl octynediol were added to the aqueous phase prior to polymerization.

TABLE III

% Acetylenic Alcohol	Visc. 20° C. SW No. 4 Cup	Freeze Thaw (3 Cycles)
0.	1' — 40"	OK
0.06	39"	OK
0.06	22"	OK
1.20	28"	Gel. 1st Cycle
1.80	29"	Gel. 1st Cycle

(The SW No. 4 Cup is similar to the well-known Ford No. 4 Cup used for viscosity determinations)

WHAT WE CLAIM IS:—

1. An aqueous phase reaction medium for emulsion polymerisation reactions comprising a dilute solution of a non-ionic protective colloid, a water-soluble non-ionic emulsifying agent containing a plurality of oxyethylene groups and characterised by a hydrophilic number (as hereinbefore defined) of 65 to 75 and one or more acetylenic ditertiary alcohols in an amount not exceeding 1% by weight of the aqueous phase.
2. An aqueous medium according to claim 1 wherein said protective colloid is a polyvinyl alcohol at least 95% hydrolysed.
3. An aqueous medium according to claim 1 or claim 2 wherein the protective colloid is present in an amount of from 1% to 10% and the emulsifying agent is present in an amount of from 0.25% to 10% each calculated by weight of the aqueous phase.
4. An aqueous medium according to any of the preceding claims wherein said acetylenic ditertiary alcohol is symmetrical.
5. An aqueous medium according to any of the preceding claims wherein said emulsifying agent is a condensation product of ethylene oxide with a polypropylene glycol of a molecular weight between 1500 and 1800 wherein the oxyethylene groups constitute from 20% to 50% of the molecule.
6. An aqueous medium according to any of claims 1 to 4 wherein the emulsifying agent is an alkyl aryl polyoxyethylene alcohol.
7. An aqueous medium according to any of the preceding claims wherein said acetylenic alcohol is dimethyl hexynediol or dimethyl octynediol.
8. A process for the production of an emulsion polymer or copolymer which comprises dispersing one or more ethylenically unsaturated monomers in an aqueous medium claimed in any of the preceding claims in the presence of a free radical polymerisation catalyst and heating the dispersion to a temperature of from 140°F. to 195°F.
9. A process according to claim 8 wherein said aqueous medium contains a catalyst promoter.
10. A process according to either of claims 8 or 9 wherein said ethylenically unsaturated monomer is vinyl acetate.
11. A process according to claim 10 wherein acrylonitrile and/or an ester of an alpha-beta-unsaturated acid is copolymerised with the vinyl acetate.
12. A process according to claim 10 or 11 wherein a vinyl aromatic hydrocarbon and/or an ester of acrylic acid is also dispersed in said aqueous medium.
13. An oil-in-water emulsion the disperse phase of which comprises a polymer of vinyl acetate or a copolymer thereof with a minor proportion of one or more other ethylenically unsaturated monomers and the continuous phase of which comprises an aqueous solution of a non-ionic protective colloid consisting of polyvinyl alcohol of at least 95% hydrolyzed quality or hydroxyethyl cellulose or admixtures thereof, a water-soluble non-ionic emulsifying agent, containing a plurality of oxyethylene groups, having a hydrophilic number (as hereinbefore defined) of from 65 to 75 and a quantity of an acetylenic, ditertiary alcohol not exceeding 1% by weight of the aqueous phase.
14. An aqueous phase reaction medium for emulsion polymerisation reactions substantially as described in any of the Examples.
15. A process for the production of aqueous

emulsions of polymers and copolymers of ethylenically unsaturated monomers substantially as described in any of the Examples.

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